Supramolecular interactions in mononuclear iron(III) complex derived from a diamide ligand: Spectroscopic and electrochemical properties

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The diamide ligand, 2,6-bis[(N-phenyl)amido]-4-methylphenol (HL), has been used to synthesize a mononuclear iron(III) complex [Fe(L)₃]-DMF and characterized by elemental analyses, IR, UV–vis spectroscopy, cyclic voltammetry and finally by X-ray crystallography. X-ray diffraction analysis reveals that the complex crystallizes in the triclinic space group P-1(2) with a = 12.4923(15), b = 13.5095(16), c = 19.296(2), α = 86.451(2), γ = 66.5850(10)°, V = 2980.1(6) Å³ and Z = 2 with the central iron(III) ion in distorted octahedral geometry. The complex shows extensive intra- and intermolecular hydrogen bonding between each molecular units as well as solvent molecules giving rise to a two dimensional assembly. It also exhibits intermolecular π–π interaction between the aromatic rings with centroid distances of around 3.55 Å. In cyclic voltammetric studies, the iron(III) complex exhibits one quasi-reversible reduction at E½ = +0.046 V versus Ag/AgCl (ΔEₚ = 0.092 V) due to a metal-centred FeIII/FeII reduction.

Keywords: Coordination chemistry, X-ray crystallography, Intermolecular hydrogen bonding, π–π stacking, Diamides, Iron

Supramolecular architectures formed by conventional covalent or coordinate covalent bonds as well as weak interactions has gained considerable attention due to their visual beauty as well as the applicability of the self-assemblies in versatile fields like optoelectronics, conductivity, charge transfer, nano-porous, magnetic, biomimetic materials, polymer science, solid-state chemistry and liquid-crystal research. These weak supramolecular interactions including strong and weak hydrogen-bonding, C–H···π, cation–π, anion–π, π···π stacking, halogen–halogen, sulfur–sulfur and gold–gold interactions are being increasingly utilized to generate self-assembled structures. In this context, suitably designed multi-dentate ligands with assorted functionalities are of utmost importance. Amide based ligands have always attracted the scientific community to explore their metallo-supramolecular chemistry. This is primarily due to the dual ability of such ligands to self-assemble through coordination bond formation in conjunction with hydrogen bonding (via amide C=O and N–H groups) capabilities.

Metal-ligand coordination provides an excellent means for the synthesis of metallo-supramolecular systems since the coordination bond is highly directional and structure of the ligand can be altered as required by established synthetic chemistry. The thermodynamic and kinetic stability can also be tuned with the suitable selection of ligand type(s) and metal ion(s). The combination of coordination chemistry of metal–ligand coordination units with non-covalent interactions such as hydrogen bonding, π–π interaction, etc., provides a powerful method for generating supramolecular architectures from simple building blocks. A typical geometry can then be extended throughout the crystal if suitable ligands that carry sites appropriate for participation in non-covalent interactions with nearest neighbours are chosen/designed.

Our group has previously reported copper(II) complex of the 2,6-bis[(N-phenyl)amido]-4-methylphenol (HL) ligand and successfully demonstrated the important role of hydrogen-bonding, C–H···π and π···π interactions in the supramolecular architecture of the metal-containing phenol-amide system. This previous work also confirms that the amide-amide hydrogen bonding increases the supramolecular complexity in the solid state. We report herein the supramolecular interactions in the mononuclear iron(III) complex derived from ligand HL. The structural, spectroscopic and electrochemical properties of this mononuclear iron(III) complex [Fe(L)₃]-DMF have also been investigated thoroughly.

Experimental
Reagent grade chemicals obtained from commercial sources were used as received. Solvents were purified and dried according to standard methods. The diamide ligand, 2,6-bis[(N-phenyl)amido]-4-methylphenol (HL) ligand were purified and dried according to standard methods. The diamide ligand, 2,6-bis[(N-phenyl)amido]-4-methylphenol (HL) ligand were purified and dried according to standard methods.

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Notes
methyl phenol\textsuperscript{24} and the amide based ligand, 2,6-bis([N-phenyl]amido]-4-methylphenol (HL) were prepared according to the previously reported method\textsuperscript{21}.

\[
\text{O} \quad \begin{array}{c}
\text{N} \\
\text{H} \\
\text{H} \\
\text{N} \\
\text{Ph}
\end{array} 
\begin{array}{c}
\text{OH} \\
\text{HN}
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\quad \text{Ph}
\]

(HL)

\textbf{Caution!} The perchlorate salt used in this study is potentially explosive and therefore should be handled in small quantities with care.

To an acetonitrile solution (25 mL) of HL (0.520 g, 1.5 mmol), were added successively acetonitrile solution (25 mL) of Fe(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O (0.232 g, 0.5 mmol) and a solution of triethylamine (0.150 g, 1.5 mmol) in acetonitrile (5 mL). The color of the solution changed from yellow to dark brown. The solution was stirred at room temperature for 30 minutes and a reddish-brown microcrystalline product precipitated. The product was collected by filtration and thoroughly washed with cold acetonitrile followed by diethyl ether. Yield: 0.360 g (62%). The X-ray quality dark brown prismatic crystals of [Fe(L)\textsubscript{2}]·DMF were grown by layering the compound in DMF with diethyl ether. Found: C, 68.04; H, 5.01; N, 8.41%. IR (KBr, cm\textsuperscript{-1}): 3430 (w, br), 3058 (w), 2920 (w), 1652 (s), 1558 (s), 1446 (s), 1387 (s), 1260 (s), 303 (s). UV-vis (in DMF, nm): 475 (6330). The perchlorate (TEAP) (0.1 M) was used as the supporting electrolyte. Cyclic voltammetric (CV) measurements were made using a three-electrode assembly comprising a platinum working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode.

Single crystals of [Fe(L)\textsubscript{2}]·DMF were mounted on glass fibers and coated with perfluoropolyether oil. Intensity data were collected at 296(2) K on a Bruker-AXS Smart Apex II diffractometer equipped with CCD detector using graphite–monochromated Mo-K\textsubscript{α} radiation (\(\lambda = 0.71073 \ \text{Å}\)). The data were processed with SAINT\textsuperscript{25} and absorption corrections were made with SADABS\textsuperscript{25} software packages. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares analysis based on \(F^2\) using WINGX software of SHELXTL\textsuperscript{26} and SHELX-97\textsuperscript{27}. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed at their geometrically calculated positions with fixed isotropic parameters. Details of crystallographic parameters,

<table>
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<th>Table 1—Crystallographic data of [Fe(L)\textsubscript{2}]·DMF</th>
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<tr>
<td><strong>Empirical formula</strong></td>
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<td><strong>No. of reflections ([I &gt; 2\sigma (I)])</strong></td>
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<td><strong>Goodness of fit, (S^a)</strong></td>
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<td><strong>Final (R_1), (wR_2) ([I &gt; 2\sigma (I)])</strong></td>
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<td><strong>(R_1), (wR_2) (all data)</strong></td>
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\(S = \left[\sum w(F_0^2 - F_c^2) / (N - P)\right]^{1/2}\) where \(N\) is the number of data and \(P\) the total number of parameters refined.

\(R_1 = \sum |F_o| - |F_c| / \sum |F_o|\).

\(wR_2(F) = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}\).
data collection and refinements for the compound are given in Table 1.

Results and discussion

The OO donor amide based ligand, 2,6-bis[(N-phenyl)amido]-4-methylphenol (HL) was prepared from di-acid chloride of 2,6-dicarboxylic-4-methyl phenol and aniline in presence of triethylamine according to Scheme 1. The white microcrystalline ligand has been characterized by elemental analysis, UV-vis, IR and $^1$H-NMR spectroscopy.

The crystalline dark–brown mononuclear iron(III) complex was obtained by the reaction between Fe(ClO$_4$)$_3·6$H$_2$O and 3 equivalents of HL in presence of triethylamine (Scheme 2).

The compound has been characterized through IR and UV-vis spectroscopy. In the IR spectrum, the compound displays a strong band at around 1650 cm$^{-1}$ which appears owing to the presence of C=N, i.e., $\nu$C=N stretching vibration of the HL ligand which is shifted toward lower wavenumber on coordination. Moreover, the electronic spectrum of the complex exhibits one sharp absorption band at 360 nm ($\varepsilon$ = 60746 M$^{-1}$ cm$^{-1}$), a shoulder at ~395 nm ($\varepsilon$ = 25800 M$^{-1}$ cm$^{-1}$) and a broad band at 475 ( $\varepsilon$ = 6330 M$^{-1}$ cm$^{-1}$) (Fig. S1), of which the first two bands are due to the internal-ligand transitions, while the third one is due to phenolate→iron(III) ligand-to-metal charge transfer transition (LMCT). The observed magnetic moment at 303 K of (I) is 5.72 BM, indicating that the iron (III) centre in the compound exists in high spin state.

The X-ray crystal structure of the mononuclear complex [Fe(L)$_3$]-DMF is shown in Fig. 1 and the selected bond lengths and bond angles are listed in Table 2. The complex crystallizes in the triclinic form with the space group $P$-1(2). The amide ligand here coordinates to the iron (III) centre in a bidentate fashion resulting in a tris-chelate complex. Though tris-chelate complexes exhibit optical isomerism (\(\Lambda\) or \(\Delta\)), the presence of both isomers in equal ratio (racemic mixture) in the lattice resulted in a non-chiral space group. The iron(III) centre of the
mononuclear complex is coordinated with three OO bidentate ligand HL leading to the formation of FeO₆ distorted octahedral geometry (Fig. 2). In the FeO₆ asymmetric unit, the iron(III) ion is coordinated with the three phenolic oxygen and three carbonyl oxygen atoms of the ligand, HL. The basal plane of the distorted octahedron is provided by O(2)O(3)O(4)O(5), while O(1) and O(6) occupy the axial positions as shown in Fig. 2. The four equatorial O atoms are nearly co-planar, the maximum deviation from the least-square plane being 0.05 Å with the iron atom located on this plane. Among the six Fe–O distances, the axial Fe–O (phenolic) bond distances of average 1.95 Å are relatively shorter than equatorial Fe–O(carbonyl/phenolic) bonds (average 2.015 Å). In addition, the cisoid angles vary from 85.68(8)° to 96.74(8)°, while the transoid angles of the iron(III) centre in the range from 169.49(8)° to 176.59(8)°, are quite unequal and most deviate significantly from the ideal value leading to the formation of distorted octahedral geometry. The packing diagram of the complex is shown in Fig. 3. It is clearly seen that one DMF solvent molecule for each molecular unit is trapped in the unit cell through intermolecular H-bonding.

Another interesting structural feature of this compound is the presence of both intramolecular and intermolecular N–H····O bonds between amide nitrogen and coordinated phenolate oxygen and uncoordinated carbonyl oxygen forming a two dimensional pattern, as shown in Fig. 4. The hydrogen atoms of the amide nitrogens, N1, N4 and N6, are intramolecularly hydrogen-bonded with phenolate oxygens O1, O4 and O6. On the other hand, each molecular unit is linked through intermolecular hydrogen-bonding between amide nitrogen N2 and N5 of one unit and the uncoordinated amide carbonyl oxygens, O8 and O9 of another molecular unit where the amide nitrogen atoms act as donors and both types of oxygens act as the acceptors. The donor-acceptor N····O distances lie between 2.623(3) and 2.862(3) Å and the N–H····O angles range from 141.00 (2)° to 160.00 (2)° (Table 3), indicating that the hydrogen bonds are very strong. It is interesting to note that each molecular unit is also connected to one solvent DMF molecule through intermolecular N–H····O bonding.

In addition, the compound reveals several intermolecular π–π interaction between the aromatic ring C1, C2, C3, C4, C5, C6 and C1′, C2′, C3′, C4′, C5′, C6′ and also between aromatic C43, C44, C45, C46, C47, C48 and C43′, C44′, C45′, C46′, C47′, C48′, respectively [the distance between

| Table 2—Selected bond distances and bond angles of [FeL₃]·DMF |
|-----------------|-----------------|-----------------|-----------------|
| Bond distances (Å) | Bond angles (°) |
| Fe(1)–O(1) | 1.9593(18) | O(1)Fe(1)O(2) | 85.68(8) |
| Fe(1)–O(2) | 2.053(2) | O(1)Fe(1)O(4) | 95.02(8) |
| Fe(1)–O(4) | 1.948(2) | O(1)Fe(1)O(5) | 91.65(8) |
| Fe(1)–O(5) | 2.036(2) | O(1)Fe(1)O(7) | 170.18(9) |
| Fe(1)–O(7) | 1.9438(18) | O(1)Fe(1)O(8) | 88.57(8) |
| Fe(1)–O(8) | 2.032(2) | O(2)Fe(1)O(4) | 96.74(8) |

Fig. 2—ORTEP representation of octahedral geometry in Fe³⁺ centres of [Fe(L)₃]·DMF showing 50% probability displacement ellipsoids.

Fig. 3—Packing diagram of [Fe(L)₃]·DMF in an unit cell.
the two pair of centroids are 3.53 and 3.61 Å, respectively] (Table 3). All these short contacts and intermolecular hydrogen-bonding give rise to a one dimensional chain structure in the molecule as shown in Fig. 4.

The electrochemical behavior of the complex [Fe(L)_3]·DMF was investigated by cyclic voltammetric techniques in DMSO using a conventional three-electrode assembly. The complex 1 is found to undergo one quasi-reversible (\(\Delta E_p = 0.092\) V) reductions at about \(E_{1/2} = +0.046\) and one irreversible reduction at about \(-0.72\) V in the potential range +0.20 to \(-1.00\) V. We have also carried out cyclic voltammetric experiments for the ligand HL in DMSO. The ligand shows a quasi-reversible reduction at about \(E_{1/2} = -0.715\) V (\(\Delta E_p = 0.20\) V). Thus, the second reduction occurs in the complex 1 due to ligand-centred process. The first reduction process observed can be assigned as Fe^{III}/Fe^{II} reduction potential. Typical cyclic voltammograms recorded in the potential range of +0.20 to \(-0.20\) V at different scan rates show that with increasing scan rate, the potential difference (\(\Delta E_p\)) also increases (Fig. 5), which confirms that the reduction wave to be quasi-reversible.

In the present study, a new iron(III) complex of a diamide ligand, 2,6-bis[(N-phenyl)amido]-4-methylphenol (HL) has been synthesized. Single crystal X-ray crystallography shows that the mono-nuclear complex contains a distorted octahedral environment with a central iron(III) cation and three OO donor ligands. Each molecular unit exhibits strong intra and intermolecular hydrogen bonding, forming one-dimensional chain. It also exhibits several intermolecular \(\pi\)–\(\pi\) interaction between the aromatic rings with centroid distances of around 3.55 Å. The electrochemical behavior reveals that the complex exhibits quasi-reversible reduction at \(E_{1/2} = +0.046\) V vs Ag/AgCl (\(\Delta E_p = 0.092\) V) due to a metal-centred Fe^{III}/Fe^{II} reduction.
Supplementary data

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 1028985). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk) or from the authors upon request. Other supplementary data associated with this article, i.e., UV-vis spectrum of [Fe(L)_3]·DMF, is available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_54A(04)478-483_SupplData.pdf.

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